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#### IX. APPENDIX I

# SAMPLING-MONITORING METHOD USING A COMBUSTIBLE GAS METER AND SAMPLING METHOD FOR USE WITH GAS CHROMATOGRAPHIC ANALYSIS

The method presented in Appendix I, Section A, is a modification of that published by the Mine Safety Appliances Company. [67] The sampling and analytical methods presented in Appendix I, Section B, and in Appendix II are based on those described by the Intersociety Committee in Methods of Air Sampling and Analysis. [68]

# Section A - Combustible Gas Meter Method

#### (a) Atmospheric Sampling

A combustible gas meter shall be used to determine acetylene concentrations in areas where exposure to acetylene is suspected. Only instruments designed for use with acetylene shall be used because other combustible gas meters may contain copper or silver wires or filaments which can form dangerous acetylides on contact with acetylene.

#### (b) Sampling Procedure

Follow the instructions given in the manual for each combustible gas meter. Typically, the sampling procedure will require the following steps:

- (1) Sweep the combustion chamber free of combustible gases and fill it with fresh air.
- (2) Turn on the batteries and apply the proper voltage to the bridge.

- (3) Balance the bridge to zero deflection on the meter while the fresh air is in the open chamber.
- (4) Draw the air sample into the meter and record the meter reading. Repeat this at least three times; calculate and record the average of the readings.
- (5) Determine the concentration of acetylene in the air samples from the calibration curve provided with each properly calibrated meter.
- (6) Record a description of sampling location and conditions, equipment used, time, and any other pertinent information.
- (7) If the concentration of acetylene as determined by this procedure is 1,500 ppm or greater, take an atmospheric sample for gas chromatography as described in Section B of this Appendix.

#### Section B - Sampling Method for Use with Gas Chromatographic Analysis

Samples shall be collected in areas where acetylene is in use and where acetylene concentrations might be expected to exceed 1,500 ppm. A description of sampling location and conditions, equipment used, time and rate of sampling, and any other pertinent information shall be recorded.

#### (a) Equipment

- (1) Rigid-walled gas sample container made of glass and fitted with stopcocks.
  - (2) One atomizer rubber bulb set or automatic buret bulb.

#### (b) Sampling Procedure

(1) Flush the container out three times using the rubber

buret bulb attached to the tube stopcock.

- (2) Collect the sample, close the stopcocks tightly, and remove the atomizer bulb.
- (3) Give the container an identifying number and record appropriate field information.
- (4) Send the samples to the laboratory for analysis as soon as possible.

#### X. APPENDIX II

#### ANALYTICAL METHOD FOR ACETYLENE

#### Principle of the Method

An aliquot of the atmospheric sample contained in the sampling container is injected into a gas chromatograph. The area of the resulting peak for acetylene is determined and compared with areas obtained from injection of a pure acetylene standard.

#### Range and Sensitivity

The lower limit of detection of this analytical procedure is 0.01 ppm/sample by volume.

#### Interferences

Any compound which has about the same retention time as acetylene under the gas chromatographic conditions described in this method, eg, methane, will interfere with the analysis. This type of interference can be alleviated by changing the operating conditions of the instrument, usually the column or the column temperature.

#### Precision and Accuracy

Replicate analyses of aliquots of uniform air samples and standards should not differ by more than 10% of the standard deviation.

## Advantages of the Method

The method is rapid and especially applicable to routine collection and analysis of grab samples. Elution of acetylene from the gas chromatograph is effected in 16 minutes or less.

#### Apparatus

- (a) Gas chromatograph equipped with a flame ionization detector and suitable sampling valve.
- (b) Column (2.4 m x 3 mm) packed with activated alumina coated with 17% (by weight) B,B'-oxydiproprionitrile. Other columns which achieve the desired separation may be used.
- (c) Mechanical or electronic integrator, or a recorder and some method for determining peak area.
- (d) Syringes: 1-ml and other convenient sizes for preparation of standards.

## Reagents

- (a) Acetylene with a guaranteed minimum purity of 99 mole%.
- (b) Bureau of Mines Grade A helium.
- (c) Hydrogen: 98.9% purity.
- (d) Pure grade nitrogen.
- (e) Pure grade air.

#### Analysis of Samples

(a) Procedure: Air samples collected in the field and returned to

the laboratory are analyzed according to the following procedure:

- (1) Turn on recorder.
- (2) Set the electrometer attenuation.
- (3) Connect the sample tube to the inlet of the sampling valve on the gas chromatograph and flush 20 ml of the sample through the loop.
  - (4) Inject a 1-ml aliquot of the sample.
  - (5) Elute the sample from the column.
- (b) Make duplicate injections of each sample and of each standard dilution used in obtaining the standard curve. No more than a 10% difference should result in the peak areas recorded for each sample.
- (c) Measure the areas of the sample peaks with an electronic integrator or by some other suitable method for area measurement.
- (d) Calculate the concentration of acetylene present in the sample directly from the standard curve. No corrections are necessary for the injected volume since it is the same for both the sample determinations and the standard curve.

#### XI. APPENDIX III

#### MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material shall be provided in the appropriate block of the Material Safety Data Sheet (MSDS).

The product designation is inserted in the block in the upper left corner of the first page to facilitate filing and retrieval. Print in upper case letters as large as possible. It should be printed to read upright with the sheet turned sideways. The product designation is that name or code designation which appears on the label, or by which the product is sold or known by employees. The relative numerical hazard ratings and key statements are those determined by the rules in Chapter V, Part B, of the NIOSH publication, An Identification System for Occupationally Hazardous Materials. The company identification may be printed in the upper right corner if desired.

#### (a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of Section I. The company listed should be a source of detailed backup information on the hazards of the material(s) covered by the MSDS. The listing of suppliers or wholesale distributors is discouraged. The trade name should be the product designation or common name associated with the material. The synonyms are those commonly used for the product, especially formal chemical nomenclature. Every known chemical designation or

competitor's trade name need not be listed.

#### (b) Section II. Hazardous Ingredients

The "materials" listed in Section II shall be those substances which are part of the hazardous product covered by the MSDS and individually meet any of the criteria defining a hazardous material. Thus, one component of a multicomponent product might be listed because of its toxicity, another component because of its flammability, while a third component could be included both for its toxicity and its reactivity. Note that a MSDS for a single component product must have the name of the material repeated in this section to avoid giving the impression that there are no hazardous ingredients.

Chemical substances should be listed according to their complete name derived from a recognized system of nomenclature. Where possible, avoid using common names and general class names, such as "aromatic amine," "safety solvent," or "aliphatic hydrocarbon," when the specific name is known.

The "%" may be the approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole mixture. This may be indicated as a range or maximum amount, ie, "10-40% vol" or "10% max wt" to avoid disclosure of trade secrets.

Toxic hazard data shall be stated in terms of concentration, mode of exposure or test, and animal used, ie, "6.8 ml/kg LD50-oral-rat," "16.4 ml/kg LD50-skin-rabbit," or "permissible exposure from 29 CFR 1910.1000," or, if not available, from other sources of publications, such as the American Conference of Governmental Industrial Hygienists or the American National Standards Institute Inc. Flammable or reactive data could be

flash point, shock sensitivity, or other brief data indicating nature of the hazard.

#### (c) Section III. Physical Data

The data in Section III should be for the total mixture and should include the boiling point and melting point in degrees Fahrenheit (Celsius in parentheses); vapor pressure, in conventional millimeters of mercury (mmHg); vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicated if by weight or volume) at 70 degrees (21.1 degrees Celsius); evaporation rate for liquids or Fahrenheit sublimable solids, relative to butyl acetate; and appearance and odor. These data are useful for the control of toxic substances. Boiling point, vapor density, percent volatiles, vapor pressure, and evaporation are useful for designing proper ventilation equipment. This information is also useful for design and deployment of adequate fire and containment equipment. The appearance and odor may facilitate identification of substances stored in improperly marked containers, or when spilled.

#### (d) Section IV. Fire and Explosion Data

Section IV should contain complete fire and explosion data for the product, including flash point and autoignition temperature in degrees Fahrenheit (Celsius in parentheses); flammable limits, in percent by volume in air; suitable extinguishing media or materials; special firefighting procedures; and unusual fire and explosion hazard information. If the product presents no fire hazard, insert "NO FIRE HAZARD" on the line labeled "Extinguishing Media."

#### (e) Section V. Health Hazard Information

The "Health Hazard Data" should be a combined estimate of the hazard of the total product. This can be expressed as a TWA concentration, as a permissible exposure, or by some other indication of an acceptable standard. Other data are acceptable, such as lowest LD50 if multiple components are involved.

Under "Routes of Exposure," comments in each category should reflect the potential hazard from absorption by the route in question. Comments should indicate the severity of the effect and the basis for the statement if possible. The basis might be animal studies, analogy with similar products, or human experiences. Comments such as "yes" or "possible" are not helpful. Typical comments might be:

Skin Contact--single short contact, no adverse effects likely; prolonged or repeated contact, possibly mild irritation.

Eye Contact--some pain and mild transient irritation; no corneal scarring.

"Emergency and First Aid Procedures" should be written in lay language and should primarily represent first-aid treatment that could be provided by paramedical personnel or individuals trained in first aid.

Information in the "Notes to Physician" section should include any special medical information which would be of assistance to an attending physician including required or recommended preplacement and periodic medical examinations, diagnostic procedures, and medical management of overexposed employees.

#### (f) Section VI. Reactivity Data

The comments in Section VI relate to safe storage and handling of hazardous, unstable substances. It is particularly important to highlight instability or incompatibility to common substances or circumstances, such as water, direct sunlight, steel or copper piping, acids, alkalies, etc. "Hazardous Decomposition Products" shall include those products released under fire conditions. It must also include dangerous products produced by aging, such as peroxides in the case of some ethers. Where applicable, shelf life should also be indicated.

#### (g) Section VII. Spill or Leak Procedures

Detailed procedures for cleanup and disposal should be listed with emphasis on precautions to be taken to protect employees assigned to cleanup detail. Specific neutralizing chemicals or procedures should be described in detail. Disposal methods should be explicit including proper labeling of containers holding residues and ultimate disposal methods such as "sanitary landfill," or "incineration." Warnings such as "comply with local, state, and federal antipollution ordinances" are proper but not sufficient. Specific procedures shall be identified.

#### (h) Section VIII. Special Protection Information

Section VIII requires specific information. Statements such as "Yes," "No," or "If necessary" are not informative. Ventilation requirements should be specific as to type and preferred methods. Respirators shall be specified as to type and NIOSH or US Bureau of Mines approval class, ie, "Supplied air," "Organic vapor canister," etc. Protective equipment must be specified as to type and materials of construction.

#### (i) Section IX. Special Precautions

"Precautionary Statements" shall consist of the label statements selected for use on the container or placard. Additional information on any aspect of safety or health not covered in other sections should be inserted in Section IX. The lower block can contain references to published guides or in-house procedures for handling and storage. Department of Transportation markings and classifications and other freight, handling, or storage requirements and environmental controls can be noted.

#### (j) Signature and Filing

Finally, the name and address of the responsible person who completed the MSDS and the date of completion are entered. This will facilitate correction of errors and identify a source of additional information.

The MSDS shall be filed in a location readily accessible to employees exposed to the hazardous material. The MSDS can be used as a training aid and basis for discussion during safety meetings and training of new employees. It should assist management by directing attention to the need for specific control engineering, work practices, and protective measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and in suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.

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MATERIAL OR COMPONEN	т	%	HAZARD DATA
	**************************************		
III P	HYSICAL D	ATA	**************************************
BOILING POINT, 760 MM HG		MELTING POINT	
SPECIFIC GRAVITY (H <sub>2</sub> O=1)		VAPOR PRESSURE	
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H2O. %	6 BY WT
% VOLATILES BY VOL		EVAPORATION RATE	(BUTYL ACETATE: 1)
APPEARANCE AND ODOR			

	IV FIRE AND	EXPLO	SION DATA	,	
FLASH POINT (TEST METHOD)			AUTOIGNITION TEMPERATURE		
FLAMMABLE LIMITS I	IN AIR, % BY VOL.	LOWER		UPPER	
EXTINGUISHING MEDIA					
SPECIAL FIRE FIGHTING PROCEDURES					
UNUSUAL FIRE AND EXPLOSION HAZARD					
	V HEALTH HA	ZARD II	NFORMATIO	N	
HEALTH HAZARD DA	ТА				
ROUTES OF EXPOSUR	IE		***************************************	-	
INHALATION					
SKIN CONTACT					
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CHRONIC OVER	EXPOSURE				
EMERGENCY AND FIR	IST AID PROCEDURES				
EYES					
SKIN					
INHALATION					
INGESTION					
NOTES TO PHYSICIAN					

VI REACTIVITY DATA
CONDITIONS CONTRIBUTING TO INSTABILITY
INCOMPATIBILITY
HAZARDOUS DECOMPOSITION PRODUCTS
CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION
VII SPILL OR LEAK PROCEDURES
STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED
NEUTRALIZING CHEMICALS
WASTE DISPOSAL METHOD
VIII SPECIAL PROTECTION INFORMATION
VENTILATION REQUIREMENTS
SPECIFIC PERSONAL PROTECTIVE EQUIPMENT
RESPIRATORY ISPECIFY IN DETAIL)
EYE
GLOVES
OTHER CLOTHING AND EQUIPMENT

IX SPECIA	AL PRECAUTIONS
PRECAUTIONARY STATEMENTS	
OTHER HANDLING AND STORAGE REQUIREMENTS	
PREPARED BY	
ADDRESS	
DATE	

# XII. TABLES

# TABLE XII-1

# PHYSICAL PROPERTIES OF ACETYLENE

Chemical formula	С2Н2
Formula weight	26.04
Boiling point	-84.0 C (sublimation occurs)
Melting point	-80.80 C
Autoignition temperatures: Pure Commercial	644 C Minimum of approximately 300 C for mixtures of 30-70% in air.
Flammable limits (by volume)	2.5-81% (in air) 2.8-93% (in oxygen)
Solubility	<pre>1.1 volumes of gas/volume of water at 15.5 C; soluble in many organic solvents</pre>
Color	Colorless
Odor	Odorless (reported odors attributed to impurities)
Specific gravity of gas at -32 C	0.6181
Vapor density at 25 C and 760 mmHg	1 mg/1 = 939 ppm

TABLE XII-2

DOMESTIC ACETYLENE CONSUMPTION

(IN MILLIONS OF POUNDS)\*

	and Esters	Acrylo- nitrile	Neoprene	Perchloro- ethylene	Trichloro- ethylene	Vinyl Acetate	Vinyl Chloride	Other	Total
1935			1		3			13	17
1936			2		5			13	20
1937			2	1	8	1		17	29
1938			3	1	6	1	1	18	30
1939			5	2	8	2	2	21	40
1940			8	2	13	2	5	25	55
1941			11	2	19	5	5	27	69
1942			17	2	30	9	12	30	100
1943			57	9	35	16	23	35	175
1944			97	12	40	18	33	43	243
1945			78	10	43	17	33	37	218
1946			81	10	43	17	47	35	233
1947			54	9	44	18	57	42	224
1948			60	_ 9	44	19	73	50	255
1949			60	10	48	18	70	43	249
1950			85	10	50	23	94	52	314
1951			100	11	58	25	101	35	330
1952	2		112	9	63	24	83	18	309
1953	3	10	137	10	75	24	104	9	372
1954	4	11	118	7	58	30	101	24	353
1955	7	39	155	8	61	39	136	25	470
1956	8	47	169	8	67	44	154	40	537
1957	10	78	188	9	66	46	162	35	594
1958	13	84	167	8	57	53	164	42	588
1959	15	103	196	8	70	64	223	29	708
1960	16	92	211	8	69	66	232	19	713
1961	19	103	186	9	58	74	229	18	696
1962	21	147	202	12	67	85	271	18	823
1963	26	171	202	11	66	114	296	18	904
1964	31	198	221	12	66	125	317	19	989
1965	41	196	220	15	77	147	339	19	1,054
1966	50	174	235	15	86	173	318	20	1,071
Convers	ion factors	in 1h acety	lene/lh prod	luot:				•	
22		Acrylonitri		-		0.6			
		Neoprene:		1935-1958		0.76			
				1959-1966		0.70			
		Perchloroetl	hylene:	1937-1953		0.22			
				1954-1966		0.17			
		Trichloroeth	nylene:	1935-1953		0.23			
				1954-1966		0.21			
		Vinyl aceta				0.33			
	,	Vinyl chlor:	ide:	1938-1951		0.46			
	from Erskine			1952-1966		0.43			

Adapted from Erskine [7]

TABLE XII-3

ACETYLENE SPECIFICATIONS

Limiting Characteristics	Grades						
	A	В	С	D	E	F	
Acetylene minimum assay, % (v/v)	95.0	98.0	98.0	98.0	99.5	99.5	
Phosphine and arsine, ppm	*	*	500	50	500	50	
Hydrogen sulfide ppm	*	*	500	50	500	50	

\*Not available

Adapted from CGA specification G-1.1 [12]

#### TABLE XII-4

#### OCCUPATIONS WITH POTENTIAL EXPOSURE TO ACETYLENE

Acetaldehyde makers Foundry workers

Acetic acid makers Glassblowers

Acetone makers Gougers

Acetylene black makers Hardeners

Acetylene production workers Heat treaters

Acrylonitrile makers Lead burners

Alcohol makers Metallizers

Braziers Metal refiners

Butadiene makers Motorboat fuel makers

Carbon black makers Organic chemical synthesizers

Ceramic makers Oxyacetylene cutters

Chloro-derivative makers Oxyacetylene solderers

Copper purifiers Oxyacetylene welders

Descalers Rubber makers

Drug makers Scarfers

Dyemakers Tetrachloroethane makers

Vinyl-derivative makers

Adapted from Gafafer [17]

TABLE XII-5
EFFECTS ON HUMANS FROM INHALATION OF ACETYLENE

Exposure Concentration	Exposure Duration	Number of Subjects	Effects	Ref-
(ppm)	20100101			
700,000 - 800,000	Up to 0.5 hr	7	Stimulated respiration	41
300,000 - 800,000	1.25 - 4.5 hr	*	Increased blood pressure	e 40
750,000			Full anesthesia	40
300,000 - 800,000	3 min - 3 hr	2,000	Complete anesthesia with no aftereffects	n 24
800,000			Narcosis in l min	24
700,000			Profuse salivation	24
200,000 - 700,000	Several hours	*	Increase (up to 50 mmHg) in blood pressure, unconsciousness in 1-2 mir	
400,000	*	* .	Insensitivity to pain in 5 min	30
350,000	*	*	Unconsciousness in 5 mir	40
330,000	*	1	Unconsciousness in 7 mir	n 28
300,000	*	1	General incoordination	28
200,000	*	1	Staggering gait	28
100,000	*	1	Slight intoxication	28

<sup>\*</sup>Not available

TABLE XII-6
EFFECTS ON ANIMALS FROM INHALATION OF ACETYLENE

Species	No.	Exposure Concentration (in Oxygen)	Effects	Ref- erence
Dogs	*	750,000 - 900,000 ppm	Anesthesia with rapid recovery, no after- effects	21
***	50	850,000 ppm	Increased respiratory volume and frequency, anesthesia with excitement and rapid recovery	45
	9	700,000 - 800,000 ppm	Decreased alkali reserve and carbonic acid blood levels, blood 02-binding capacity and arterial 02 deficit higher during and lower after anesthesia, slightly increased blood sugar during anesthesia	53, 54
11	*	500,000 ppm	Rapidly induced anes- thesia with no excitement	44
Cats	*	800,000 ppm	Slightly raised blood pressure	48
11	*	400,000 - 800,000 ppm	Reduced respiration, slightly raised blood pressure	41
***	*	200,000 - 800,000 ppm	Slightly raised blood pressure	50
11	*	Up to 800,000 ppm	н	

TABLE XII-6 (CONTINUED)

#### EFFECTS ON ANIMALS FROM INHALATION OF ACETYLENE

Species	No.	Exposure Concentration (in Oxygen)	Effects	Ref- erence
Rabbits	*	600,000 - 800,000 ppm	Reduced respiration, slightly raised blood pressure	41
11	*	Up to 700,000 ppm	Increased respiration after anesthesia, decreased arterial blood CO2 tension and CO2-combining power	52
Not specified	*	250,000 ppm	Slight capillary hyper- emia	47
***	*	500,000 ppm**	After 5-10 min, death	27
11	*	250,000 ppm**	After 30-60 min, toxicity	27
11	*	100,000 ppm**	Toleration for 30-60 min	27

\*Not available

<sup>\*\*</sup>In air

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